

a partially *cis*-configuration.<sup>1</sup> This statement refers to flowers which have developed fully under natural conditions on the intact plant. In recent experiments it was found, however, that, if stems with buds were placed in water for several days and exposed only to diffuse light in the laboratory at room temperature, the flowers were noticeably different in tint and paler in color than flowers which developed on the intact plant in the open. Parallel chromatograms of extracts of the two materials established the fact that under these two sets of conditions, the polyene pigment mixtures differed both qualitatively and quantitatively with respect to the components found. The paler flowers contained a greater number of lycopene stereoisomers than the controls. The chromatogram of the paler flowers included considerable quantities of polycopene, C<sub>40</sub>H<sub>56</sub>, and pro- $\gamma$ -carotene, C<sub>40</sub>H<sub>56</sub>. The spectral maxima of these pigment fractions in petroleum ether (b. p. 60–70°) were 467, 440 m $\mu$  and 461, 431 m $\mu$ , respectively. Upon addition of iodine to the solutions, the bands showed the characteristic shift to 500.5, 469.5, 440 m $\mu$  and 494, 461 m $\mu$ . Both pro-carotenoids have been identified by mixed chromatograms with samples from other sources.

In the light of the above observation, it is possible that polycopene and pro- $\gamma$ -carotene are precursors of lycopene and  $\gamma$ -carotene in the biosynthesis of the *Mimulus* pigment.

(1) L. Zechmeister, A. L. LeRosen, F. W. Went and L. Pauling, *Proc. Nat. Acad. Sci.*, **27**, 468 (1941); A. L. LeRosen and L. Zechmeister, *This Journal*, **64**, 1075 (1942); L. Zechmeister and W. A. Schroeder, *ibid.*, p. 1173.

GATES AND CRELLIN LABORATORIES OF CHEMISTRY  
CALIFORNIA INSTITUTE OF TECHNOLOGY  
PASADENA, CALIFORNIA RECEIVED JULY 1, 1942

### Some Physical Constants of N-Octyl-, N-Dodecyl- and N-Cetyl-piperidine

By F. H. STROSS AND R. J. EVANS

There exists little available information on the physical properties of the higher N-alkyl-piperidines. When, in the course of an investigation, it became necessary to prepare N-cetyl-piperidine, only two references<sup>1,2</sup> were found which mentioned this compound. Its ionization constant was found to be surprisingly low in comparison with the known constants of the lower homologs,

(1) P. Karrer, F. W. Kahnt, R. Epstein, W. Jaffe and T. Ishii, *Helv. Chim. Acta*, **21**, 233 (1938).

(2) H. W. Magnusson and E. R. Schierz, *Univ. of Wyoming, Publications VII*, 1–11 (1940).

and, therefore, the N-dodecyl- and N-octyl-piperidines were also prepared and their characteristic properties measured. The results are given in Table I.

TABLE I  
PHYSICAL CONSTANTS OF N-OCTYL, N-DODECYL AND N-CETYL PIPERIDINES

Piperidines	N-Octyl	N-Dodecyl	N-Cetyl
M. p., °C.	..	..	21
B. p. { °C.	89 112 122	141 161	176–177
{ Mm.	1 6 10	1 5	1
$d_{20}^{20}$	0.8324	0.8378	0.8468
$n_D^{20}$	1.4544	1.4588	1.4620
N, % { Calcd.	7.1	5.5	4.5
{ Found	6.9 7.0	5.5	4.4
Mol. wt. { Calcd.	197.4	253.5	309.6
{ Found	197	253	304
$pK_H$ at 27°C.	8.28	5.92	5.8

While the N-cetyl and N-dodecyl compounds are weak bases of a strength close to that of pyridine, N-octylpiperidine occupies a position intermediate between the higher homologs and the N-methyl- to butylpiperidines. The latter are almost as strong bases as the unsubstituted piperidine, which has a  $pK_H$  of 11.1 at 25°.

The bases were prepared by the method described by Magnusson and Schierz.<sup>2</sup> Aqueous piperidine was refluxed with a slight excess of the alkyl iodide, while an excess of potassium hydroxide was gradually added. The upper of the two layers formed during refluxing was fractionally distilled over solid potassium hydroxide at 2 mm. pressure, yielding a clear distillate. The cetyl-piperidine was yellow, the dodecyl compound had a slight yellow tinge, and the octyl-piperidine was colorless. The analyses were made and the constants determined after redistilling these products.

SHELL DEVELOPMENT CO.  
EMERYVILLE, CALIFORNIA RECEIVED AUGUST 11, 1942

### Empirical Heat Capacity Equations of Gases

By HUGH M. SPENCER AND GORDON N. FLANNAGAN

Since the publication of empirical heat capacity equations of simple gases,<sup>1</sup> values of thermodynamic functions for many gases have been derived from spectroscopic data.<sup>2</sup> In the case of

(1) Hugh M. Spencer and John L. Justice, *This Journal*, **56**, 2311 (1934). The heat capacities of bromine and equilibrium chlorine are better represented by equations of form (2). The constants  $a$ ,  $b \times 10^3$ ,  $c' \times 10^{-5}$ , maximum and average percentage deviations are 8.911, 0.140, -0.0298, 0.09, 0.02 and 8.764, 0.271, -0.656, 0.24 and -0.11, respectively.

(2) E. B. Wilson, Jr., *Chem. Rev.*, **27**, 17 (1940).

TABLE I<sup>a</sup>

Compound	Source	Range, °K.	<i>a</i>	<i>b</i> × 10 <sup>3</sup>	<i>c</i> × 10 <sup>7</sup>	<i>c'</i> × 10 <sup>-6</sup>	<i>d</i> × 10 <sup>9</sup>	% Deviation Max. Average
Acetylene	3	273.1-1273.1	11.942	4.387		-2.322		1.28 0.48
Ammonia <sup>b</sup>	4	291.16-1000	6.189	7.887	- 7.28			0.65 .23
Bromoform	5	298.1-600	9.356	32.319	- 212.72			.17 .11
Bromomethane	5	298.1-1200	4.184	22.445	- 74.96			.66 .33
<i>i</i> -Butane <sup>c,d</sup>	6	298.1-1500	2.296	82.407	- 287.92			.54 .29
<i>n</i> -Butane <sup>c,d</sup>	6	298.1-1500	2.247	81.718	- 286.13			.29 .15
Carbon dioxide	7	300-1500	6.369	10.100	- 34.05		2.260	2.07 .62
Carbon dioxide	7	300-1500	5.166	15.177	- 95.78			0.35 .15
Carbon disulfide	8	298.1-1800	13.289	0.862		-2.502		1.86 .79
Carbon disulfide	8	298.1-1800	7.692	13.426	- 91.16		2.112	1.04 .41
Carbon oxysulfide	8	298.1-1800	12.288	1.321		-2.630		2.06 .94
Carbon oxysulfide	8	298.1-1800	6.554	13.880	- 88.18		1.964	1.19 .44
Carbon tetrabromide	5	298.1-600	15.238	28.987	- 225.76			0.21 .14
Carbon tetrachloride	9	273.1-773.1	22.675	3.274		-3.264		.57 .24
Chloroform	9	273.1-773.1	7.052	35.598	- 216.86			.69 .30
Chloromethane	9	273.1-773.1	3.563	22.998	- 75.71			.64 .24
Chlorotribromomethane <sup>f</sup>	10	250-600	12.917	36.565	- 294.64			.50 .23
Cyanogen <sup>f</sup>	4	291.16-1000	9.892	14.484	- 62.07			.74 .45
Deuteroformaldehyde <sup>g</sup>	11	291.16-1500	4.419	17.540	- 57.48			1.00 .42
Dichlorodibromomethane	10	250-600	12.902	34.713	- 265.10			1.01 .27
Dibromomethane	13	298.1-600	5.244	31.809	- 177.09			0.12 .06
Dichloromethane	10	250-600	4.309	31.673	- 163.51			.27 .08
Difluoromethane <sup>h</sup>	10	250-600	4.203	21.623	- 40.88			.95 .34
Diiodomethane	10	250-600	5.839	32.571	- 195.28			.13 .06
Ethyl alcohol <sup>i</sup>	12	300-1000	3.578	49.847	- 169.91			.28 .15
Ethane <sup>j</sup>	4	291.16-1000	1.375	41.852	- 138.27			.76 .26
Ethylene <sup>k</sup>	15, 4	291.16-1500	2.706	29.160	- 90.59			1.46 .92
Formaldehyde <sup>l</sup>	11	291.16-1500	4.498	13.953	- 37.30			1.90 .73
Fluorochloromethane	10	250-600	4.292	27.025	- 106.05			0.57 .21
Fluoromethane	13	298.1-600	3.616	18.239	- 20.35			.89 .32
<i>n</i> -Heptane <sup>c,d</sup>	6	298.1-1500	5.401	136.930	- 487.71			.23 .13
<i>n</i> -Hexane <sup>c,d</sup>	6	298.1-1500	4.296	118.661	- 421.30			.28 .12
Hydrogen cyanide <sup>o</sup>	14	300-1000	5.974	10.208	- 43.17			.23 .13
Hydrogen sulfide <sup>m</sup>	15, 16	298.1-1800	6.385	5.704	- 12.10			2.00 .50
Hydrogen sulfide <sup>m</sup>	15, 16	298.1-1800	6.955	3.675	+ 7.40		-0.585	1.02 .37
Iodomethane <sup>n</sup>	13	298.1-600	4.105	24.487	- 97.33			0.14 .07
Methane <sup>o</sup>	15, 4	291.16-1500	3.422	17.845	- 41.65			2.59 .97
2-Methylbutane <sup>c,d</sup>	6	298.1-1500	2.801	102.820	- 367.41			0.67 .35
Methyl cyanide	4	291.16-1200	5.018	27.935	- 93.02			.40 .21
Nitrous oxide	7	298.1-1500	6.529	10.515	- 35.71			1.26 .68
<i>n</i> -Octane <sup>c,d</sup>	6	298.1-1500	6.231	155.942	- 558.57			0.24 .14
<i>n</i> -Pentane <sup>c,d</sup>	6	298.1-1500	3.140	100.532	- 355.60			.32 .16
Phosgene	11	291.16-1000	16.051	2.894		-2.159		.59 .31
Phosphine <sup>c</sup>	17	298.1-1500	4.496	14.372	- 40.72			.29 .13
Phosphorus (diatomic) <sup>c</sup>	17	298.1-1500	8.643	0.202		-1.030		.13 .05
Phosphorus (tetraatomic) <sup>c</sup>	17	298.1-1500	19.227	0.509		-2.975		.18 .08
Phosphorus oxychloride	17	298.1-1000	23.294	2.185		-3.534		.18 .07
Phosphorus pentachloride <sup>p</sup>	17	298.1-500	4.739	107.329	- 1192.00			.05 .02
Phosphorus tribromide <sup>c,d</sup>	17	298.1-800	18.154	2.045		-0.153		.05 .02
Phosphorus trichloride <sup>c</sup>	17	298.1-1000	20.068	-0.289		-2.706		.34 .11
Phosphorus trifluoride <sup>c,q</sup>	17	298.1-1000	17.559	1.972		-4.569		.17 .13
Propane <sup>c,d</sup>	6	298.1-1500	0.410	64.710	- 225.82			.73 .27
Sulfur dioxide	8	298.1-1800	11.895	1.089		-2.642		3.18 1.31

(3) E. Justi, "Spezifische Wärme, Enthalpie, Entropie und Dissoziation technischer Gase," J. Springer, Berlin, 1938, p. 150.

(4) H. W. Thompson, *Trans. Faraday Soc.*, **37**, 344 (1941).(5) D. P. Stevenson and J. Y. Beach, *J. Chem. Phys.*, **6**, 25 (1938).(6) K. S. Pitzer, *Chem. Rev.*, **27**, 39 (1940).(7) L. S. Kassel, *This Journal*, **56**, 1938 (1934).(8) P. C. Cross, *J. Chem. Phys.*, **3**, 825 (1935).(9) R. D. Vold, *This Journal*, **57**, 1192 (1935).(10) G. Glockler and W. F. Edgell, *Ind. Eng. Chem.*, **34**, 532 (1942).(11) H. W. Thompson, *Trans. Faraday Soc.*, **37**, 251 (1941).(12) J. G. Aston, *Ind. Eng. Chem.*, **34**, 514 (1942).(13) W. F. Edgell and G. Glockler, *J. Chem. Phys.*, **9**, 484 (1941).(14) A. R. Gordon, *ibid.*, **5**, 30 (1937).(15) E. B. Wilson, Jr., *ibid.*, **4**, 526 (1936).(16) P. C. Cross, *ibid.*, **3**, 168 (1935).(17) D. P. Stevenson and D. M. Vost, *ibid.*, **9**, 403 (1941).

TABLE I (Concluded)

Compound	Source	Range, °K.	a	b × 10 <sup>8</sup>	c × 10 <sup>7</sup>	c' × 10 <sup>-5</sup>	d × 10 <sup>9</sup>	% Deviation	
								Max.	Average
Sulfur dioxide	8	298.1-1800	6.147	13.844	- 91.03		2.057	0.43	.23
Sulfuryl chloride <sup>r</sup>	18	291.16-450	8.557	43.918	- 353.57			.05	.03
Tetramethylmethane <sup>c,d</sup>	6	298.1-1500	1.340	109.879	- 411.71			.55	.28
Tetramethylmethane <sup>c,s</sup>	19	300-1500	6.076	98.954	- 353.69			.16	.06
Thiophosgene <sup>t</sup>	11	291.16-1000	17.773	1.750		-2.556		.62	.33
Thiophosphoryl chloride <sup>c,d,u</sup>	17	298.1-1000	23.923	1.968		-3.114		.48	.16
Trichlorobromomethane	10	250-600	11.462	39.983	- 318.76			.57	.24
Water <sup>v</sup>	15, 20, 21	298.1-1500	7.219	2.374	+ 2.67			.96	.40

<sup>a</sup> For a number of gases the heat capacities cited in the references are incorrect at one or more temperatures. New values for these, based on the same wave numbers, have been calculated, and are indicated as in Note b. <sup>b</sup> Rotational distortion correction amounting to  $0.058 \times 10^{-3}T$  has not been included. At 500°K. for  $C_p^0 = 10.14$ , read 9.92. <sup>c</sup> Percentage deviation tested with respect to mean heat capacity. <sup>d</sup> Several heat capacity measurements by K. S. Pitzer (THIS JOURNAL, 63, 2413 (1941)) have caused him to doubt the correctness of the frequencies used in ref. 6. <sup>e</sup> At 250°K. for  $C_p^0 = 20.11$ , read 20.12. <sup>f</sup> At 450°K. for  $C_p^0 = 15.23$ , read 15.24. <sup>g</sup> At 650°K. for  $C_p^0 = 13.53$ , read 13.48. <sup>h</sup> At 350, 550 and 600°K. for  $C_p^0 = 10.22$ , 14.93 and 15.66, read 11.22, 14.88 and 15.65, respectively. <sup>i</sup> The values of the mean heat capacity to 400, 700 and 1000° were neglected in setting up and testing the equation. <sup>j</sup> At 700°K. for  $C_p^0 = 24.33$ , read 24.05. <sup>k</sup> At 700°K. for  $C_p^0 = 18.3$ , read 18.83. The rotational distortion correction ( $0.031 \times 10^{-3}T$ ) has not been included. <sup>l</sup> At 650 and 1200°K. for  $C_p^0 = 12.07$  and 15.92, read 12.00 and 15.88, respectively. <sup>m</sup> Rotational distortion correction amounting to  $0.064 \times 10^{-3}T$  has been included. <sup>n</sup> At 350°K. for  $C_p^0 = 11.48$ , read 11.47. <sup>o</sup> The rotational distortion correction ( $0.068 \times 10^{-3}T$ ) has not been included. <sup>p</sup> Only three values of the mean heat capacity were available; these were solved simultaneously. <sup>q</sup> The mean heat capacity (298.1-350) was excluded. <sup>r</sup> Simultaneous solution at  $T = 300, 380$  and  $450^\circ\text{K}$ . <sup>s</sup> Graphically extrapolated values of mean heat capacity at 400, 500 and 600 were used in setting up and testing the equation. <sup>t</sup> At 400 and 650°K. for  $C_p^0 = 16.68$  and 18.45, read 16.78 and 18.38, respectively. <sup>u</sup> The two largest deviations are for temperatures for which the theoretical values do not fall on the curve. <sup>v</sup> Rotational distortion correction based on ref. 21, amounting to  $0.092 \times 10^{-3}T$ , has been included. The correction based on Wilson's<sup>15</sup> theoretical value derived from the force constants of the molecule would have been  $0.081 \times 10^{-3}T$ .

several triatomic gases more complete spectroscopic data have been treated by more satisfactory statistical mechanical methods. Though it is still necessary to consider the polyatomic (including some triatomic) molecules as harmonic oscillators, thermodynamic data based on this conception have proved to be of satisfactory, though not absolute, accuracy. Use of the normal coordinate analysis of vibrations, the assignment of potential barriers due to hindered rotations by reference to thermochemical data at one or more temperatures, and the methods of extrapolation to closely related molecules have further increased the useful applications of this method.

The same remarks concerning the usefulness of empirical heat capacity equations for these gases might be made as were made in the earlier paper.<sup>1</sup>

Table I presents the equations and the percentage deviations of such equations representing the heat capacities of the various gases in the forms

$$C_p^0 = a + bT + cT^2 \quad (1)$$

$$C_p^0 = a + bT + c'/T^2 \quad (2)$$

$$C_p^0 = a + bT + cT^2 + dT^3 \quad (3)$$

Except as indicated in the notes to Table I, equations of the forms (1) and (2) have been ob-

(18) H. W. Thompson, *Trans. Faraday Soc.*, **37**, 340 (1941).

(19) J. G. Aston, *Chem. Rev.*, **27**, 59 (1940).

(20) A. R. Gordon, *J. Chem. Phys.*, **1**, 308 (1933).

(21) C. C. Stephenson and H. O. McMahon, *ibid.*, **7**, 614 (1939).

tained as least square solutions of all the data in appropriate forms of heat capacity or mean heat capacity. Depending on the relative contributions of the various wave numbers over the range of temperatures concerned, one or the other of forms (1) and (2) are to be preferred. If the change of curvature with respect to the horizontal ( $T$ ) axis is greater at the higher temperatures of a given range form (1) is preferable, and *vice versa*. In some instances the range of temperatures is relatively so great that comparatively large deviations from the most appropriate three-constant equation occur.<sup>22</sup> Adjusted simultaneous solutions of form (3) are offered for these. It should be noted that empirical equations are unreliable for extrapolation.

The original articles must be consulted to ascertain the bases of the theoretical values which the equations represent. As in most of the original publications constants of the "International Critical Tables" have been used.

COBB CHEMICAL LABORATORY  
UNIVERSITY OF VIRGINIA  
CHARLOTTESVILLE, VA.

RECEIVED JULY 11, 1942

(22) For one gas, carbon dioxide, a three-constant equation has been derived [R. L. Sweigert and M. W. Beardsley, Georgia School of Tech. State Eng. Expt. Sta. Bulletin No. 2 (1938)] involving  $T^0$ ,  $T^{-1}$  and  $T^{-2}$  terms, which more accurately represents the values derived from spectroscopic data than do three-constant equations of forms (1) or (2).